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14. ABSTRACT The objective of this DURIP program is to develop an integrated instrumentation package that combines the capability of performing accurate and complete materials evaluation and shortening the time required to make critical characterization information available to device engineers and DoD program managers. The facility established in this program is capable of efficiently and systematically characterizing electrical and optical properties of organic conjugated oligomers and polymers for LEDs, solid state lasers, two-photon absorption, and photovoltaic cell applications.					
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END-OF-THE-YEAR-REPORT

for

GRANT #, F49620-01-1-0259

**Instrumentation Facility for the Evaluation of Photonic and
Opto-electronic Materials**

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November 20, 2002

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1. Introduction

Organic materials and hybrid organic/inorganic materials have the potential to play key roles in modern technology related to American defense and civilian economy. In particular, they have the potential for being the materials of choice for applications ranging from integrated optical circuits to sensor protection to display technology. In the area of integrated optical circuits (critical for the insertion of photonic technology into advanced systems), organic polymeric materials can be used for low-loss passive and infrared waveguides, electro-optic switches and high speed modulators, and integrated optical components such as wavelength filters, channel dropping filters, and power combiners. Furthermore, organic conjugated molecules and polymers can be used to fabricate highly efficient, full color displays and optically-pumped lasers utilizing the broad spectral range of emission colors available from these materials. Inherent to these applications is the ease of fabricating complex waveguide circuits or pixels over relatively large areas; the ability to build devices on almost any substrate including pre-processed semiconductor electronics; and the relatively wide range of materials properties (index of refraction, electrical conductivity, etc.) that are available or can be engineered into compatible systems. Moreover, organic materials are readily adaptable to nanoscale architectures which can, in turn, be used to enhance device response such as optical limiting. For example, amplification of inherent material optical limiting and lasing through dendrimer, block copolymers, and photonic bandgap architectures may permit critical reduction in the threshold for limiting and lasing, permitting wide scale implementation of new technology.

The first electrically pumped organic diode laser was achieved at the Bell Laboratories [Batlogg & co-workers, *Science*, **289**, 599-601 (2000)]. The threshold and other lasing characteristics of the organic diode lasers made from single-crystal thin films of pentacene were found to be comparable or superior to the best current inorganic semiconductor lasers. These initial results suggest the great potential in developing low power solid state light sources from high quality organic materials and nanostructures. Because pentacene and related polyacenes are very sensitive to oxygen and ambient moisture, development of other more stable conjugated oligomers or polymers will be essential to make organic diode lasers practical.

To realize this goal, the greatest challenge for scientists in this field is to find suitable electroluminescent (EL) material systems (light emitter, electron and hole transporters) which possess efficient and balanced charge injection/transport to ensure low operating voltages and high quantum efficiencies. In addition, they need to sustain high transient current densities (10^3 A/cm²) for electrical pumping and have good mechanical properties for multi-layer integration. Furthermore, it is essential not only to minimize excited-state absorption so as to enhance optical gain but also to improve the design of lasers with either a high-Q resonant cavity or a waveguiding structure to reduce the lasing threshold. To date, many studies have been performed on optimizing one or several of the required properties. However, no single polymer has met the requirements necessary for electrically-pumped lasing.

In principle, an EL polymer requires the injection of holes and electrons into the emitter layer. The recombination of the injected electrons and holes in the polymer layer generates singlet excitons whose radiative decay produces visible light. The characteristics of an EL polymer are determined by the tunneling of both holes and electrons through the interface barriers which is caused by the band offset between the electroluminescent polymer and the

electrodes. A significant difference in the barrier height at the polymer/cathode and polymer/anode interfaces results in unbalanced hole and electron injections and therefore dramatically reduces the photon/electron quantum efficiency of the devices. In order to achieve higher device efficiency, highly luminescent polymers must be chosen, ultimate control of the metal-on-polymer interface, and balanced charge (hole and electron) injection are all considered to be crucial.

Although different groups are developing the basic luminescent molecules, polymeric materials, processes, and devices, they measure and report their results based on different specific and individual tests. Due to the different test procedures and measurement methods, it is difficult to make comparisons between the materials. Thus, selecting the most promising development path becomes difficult. To speed up the tedious selection process, it is highly desirable to have an integrated instrumentation that provides the necessary information such as charge mobility, brightness, linear and circular polarized photo- and electro-luminescence emissions, light polarization, current-electric field characteristics, and thresholds of optically pumped lasing, in a short time span. In addition, information and structure/property relationships developed during this process will be very beneficial for the material and device development for light-harvesting, light-detection, and light amplification.

2. Objective

The objective of this DURIP program is to develop an integrated instrumentation package that combines the capability of performing accurate and complete materials evaluation and shortening the time required to make critical characterization information available to device engineers and DoD program managers. The facility established in this program is capable of efficiently and systematically characterizing electrical and optical properties of organic conjugated oligomers and polymers for LEDs, solid state lasers, two-photon absorption, and photovoltaic cell applications. It combines the capability of performing the measurements of charge mobility, conductivity, linear and circular polarized photo- and electro-luminescence emission spectra, luminous efficiencies, the thresholds of gain narrowing from optical pumping, as well as cross-section for two-photon absorbing chromophores. In addition, the instrumentation interfaces very well with the existing facility for performing LED and electro-optic materials research at UW. This laboratory consolidates capabilities which we have developed and which are currently being heavily used by researchers at DoD laboratories and by industry (as well as by academic researchers from a number of universities) and will assure the cost effective operation of the facility. The development of a complete material system for the above applications will demonstrate the usefulness of the procedure and instrumentation.

3. Impact to the new research programs on organic electronics and photovoltaic materials at University of Washington

The established instrumentation facility greatly enhances the quality and capability of the LED/plastic laser and photovoltaic material research programs at the University of Washington (UW) to evaluate suitable material system properties. The research programs established by Professors Alex Jen and Larry Dalton possess the capability of synthesizing, characterizing, and fine-tuning the properties of novel functional polymers. Recent exciting results from the LED

material development at Professor Jen's group have shown excellent light-emitting and charge-transporting properties. Polymers with very low turn-on voltages (as low as 2.2 V), extremely high external quantum efficiencies ($> 6\%$), luminous efficiency (25 lm/W at 100 cd/m²), and high brightness ($> 60,000$ cd/m²) have been achieved. The combined properties of these polymers have provided a great material foundation for the development of highly efficient LEDs, plastic lasers, and photovoltaic cells.

UW's current facility possesses the capability of measuring conductivity and electro-activity (such as redox potentials/reversibility of the polymers by using cyclic voltammetry) of polymers. For polymer characterization, this facility is equipped with instruments such as FT-IR, UV-Vis-Near IR and FT-NMR for chemical structure identification; TGA and DSC for thermal analysis; GPC and HPLC for polymer dual-head thin film evaporator in dry box for evaporating metals and small organic molecules with controlled thickness; and Dektak instrument for measuring thin film thickness. In addition, UW has state-of-the-art clean room in its microfabrication laboratory that can provide the needed lithography and fabrication of photonic and opto-electronic devices. The instrumentation facility established through this program helps to guide the synthetic effort for fine-tuning the properties of polymers and establishing desirable light-emitting, lasing, and light-harvesting material system properties, and thus, directly impact the fabrication of highly efficient devices.

4. Interface between the instrumentation and the existing facility for electro-optic (E-O) and light-emitting materials research at University of Washington

This integrated instrumentation interfaces very well with the existing E-O and LED materials research facility at UW to provide strong capability for evaluating organic photonic/opto-electronic material properties. One of the new research program proposed by both professors Jen and Dalton aims at demonstrating an integrated all polymer LED/E-O device by using organic conjugated polymers as both a light source (plastic laser) and a photodetector, and using NLO polymer channel waveguides as an E-O switching device. This instrumentation greatly enhances the capability of quickly developing/screening both LED and E-O materials systems to ensure the greatest chance of success. In the area of polymer characterization, the facility at NU is equipped with the instruments such as TGA and DSC for thermal analysis; GPC and HPLC for polymer molecular weight measurement; and Dektak instrument for measuring thin film thickness. In addition, FT-IR and UV-Vis-Near IR spectrometer were used to determine the thermal stability of the E-O polymer thin films. In the areas of optical and electrical characterization, the micromanipulator device could be used to cure (up to 400 °C) and pole NLO thin films and channel waveguides; Metricon prism coupler could measure refractive index, optical loss, and thickness of polymer thin films; lock-in amplifier and the associated electronic system could measure optical and electro-optic signal generated by LED/E-O materials. This integrated instrumentation facility helps to bridge between the effort of evaluating E-O and LED polymeric material system properties, and thus, directly impacts the fabrication of all polymer laser devices.

5. Research training of students

The highly interdisciplinary nature of this program in developing high-performance light-emitting materials for LED/laser device applications, the outstanding faculty and institutions

involved, and connections with high technology device companies and DoD laboratories ensure a rich educational environment for the graduate students, postdoctors, and undergraduate students involved. Students are active members involved in closely integrated material synthesis, characterization, and device fabrication. Students associated with this program will emerge with a unique background and complement of skills. The ability to communicate with and work with academic, government, and industrial researchers in other disciplines towards a common goal will uniquely qualify them for the technical workforce of the future.

6. Papers published that acknowledge the AFOSR

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2. "A Novel Bipolar Electroluminescent Poly (aryleneethynylene) Consisting of Carbazole and Diethynylthiophene units", X. Zhan, Y. Liu, D. Zhu, X. Jiang, and A. K-Y. Jen, Macromolecular Chem. Phys., **2001**, *202*, 2341.
3. "Synthesis and Characterization of Processible Electroluminescent Poly [(2,7-Fluorenyl eneethynylene)-alt-co-(2,5-Thienyleneethynylene)", X. Zhan, Y. Liu, D. Zhu, X. Jiang, A. K-Y. Jen, Synth. Metals., **2001**, *124*, 323.
4. "Synthesis and Characterization of Quinoline-Based Copolymers for Light Emitting Diodes", Y. Liu, H. Ma, and A. K-Y. Jen, J. Mater. Chem., **2001**, *11*, 1800.
5. "Functional Dendrimers for Nonlinear Optics", H. Ma and A. K-Y. Jen, Adv. Mater., **2001**, *13(15)*, 1201.
6. "Dispersion of the First Molecular Hyperpolarizability of Charge-Transfer Chromophores Studied by Hyper-Rayleigh Scattering", J. N. Woodward, C. H. Wang, and A. K-Y. Jen, Chemical Physics, **2001**, *271*, 137.
7. "A Binaphthyl-Bithiophene Copolymer for Light-Emitting Devices", Y. Liu, A. K-Y. Jen, G. Yu, Q. Hu, and L. Pu,, Macromolecular Chemistry and Physics, **2002**, *203*, 37.
8. "Photostability of Electro-optic Polymers Possessing Chromophores with Very Efficient Amino Donors and Cyano-containing Acceptors", A. Galvan-Gonzalez, G. Stegeman, A. K-Y. Jen, X. Wu, M. Canva, A.C. Kowalczyk, X. Q. Zhang, and H. S. Lackritz, J. Opt. Soc. Am. B., **2001**, *18(12)*, 1846.
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11. "The Effect of Ligand Conjugation Length on Europium Complex Performance in Light-Emitting Diodes", X. Jiang, A. K-Y. Jen, D. Huang, T. M. Londegan, G. D. Phelan, L. R. Dalton, Synthetic Metals, **2002**, *125*, 331..
12. "High-Performance Exciplex Emission from Polymer Light-Emitting Diodes Based on Hole-Transporting Amine Derivatives and Electron-Transporting Polyfluorenes", X. Jiang, M. S. Liu, and A. K-Y. Jen, J. Appl. Phys., **2002**, *91(12)*, 10147.
13. "Efficient Cyano-containing Electron-Transporting Polymers for Light-Emitting Diodes", M. S. Liu, X. Jiang, P. Herguth and A. K-Y. Jen, Chem. Mater., **2001**, *13*, 3820.

14. "Highly Efficient and Thermally Stable Organic/Polymeric Electro-optic Materials by Dendritic Approach", A. K-Y. Jen, H. Ma, T. Sassa, S. Liu, S. Suresh, L. R. Dalton, and M. Haller, Proc. SPIE, **2001**, 4461, 24,
15. "Effect of Cyano-Substituents on Electron Affinity and Electron-Transporting Properties of Conjugated Polymers", M. S. Liu, X. Jiang, S. Liu, P. Herguth, and A. K-Y. Jen, Macromolecules, **2002**, 35, 3532.
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22. "Red Emitting Electroluminescent Devices Based on Osmium Complexes Doped Blend of Poly(vinylnaphthalene) and 1,3,4-Oxadiazole derivative", X. Jiang, A. K-Y. Jen, B. Carlson and L. R. Dalton, Appl. Phys. Lett., **2002**, 81(17), 3125..
23. "Polymer-Based Optical Waveguides: Materials, Process, and Devices", H. Ma, A. K-Y. Jen, and L. R. Dalton, Adv. Mater., **2002**, 14(19), 1339..

Budget:

Z-scan Measurements

EQUIPMENTS	MODEL	UNIT PRICE	TOTALS	VENDER AND ADDRESS
Translation Stage Driver	UTM50Pp1HL 25792-01	\$3,046 \$600		Newport Corporation Attn: Order Entry Department P.O. Box 19607 Irvine, CA 92713-9607 Tel: 800-222-6440 Fax: 949-253-1680
subtotal			\$3,646	
Photo Detector Photo Detector	818-BB-22 818-BB-22	\$389 \$389		Newport Corporation Attn: Order Entry Department P.O. Box 19607 Irvine, CA 92713-9607 Tel: 800-222-6440 Fax: 949-253-1680
subtotal			\$778	

Beam Expander	T81-3X	\$475		Newport Corporation Attn: Order Entry Department P.O. Box 19607 Irvine, CA 92713- 9607 Tel: 800-222-6440 Fax: 949-253-1680
subtotal			\$475	
Dimension CL, X-Y Closed-loop SPM Microscope Head	DAFMCL	\$40,000	\$40,000	Veeco Metrology Group 112 Robin Hill Road Santa Barbara, CA 93117 Tel: 805-967-1400 Fax: 800-873-9750
subtotal				
Autocorrelator	FR-103MN			Femtochrome Research 2123 4th St. Berkley, CA 94710 Tel: 510-644-1869 Fax: 510-644-0118
subtotal		\$8,000	\$8,000	
Computer	Dimension L (E-VALUE CODE: 6V908-500815o)	\$2,168		Dell Computer Corporation One Dell Way Round Rock, Texas 78682 Tel: 800-626-8286 Fax: 800-365-5329
subtotal			\$2,168	
GPIB Controller GPIB Cable	777158-01 763061-02	\$495 \$85		National Instruments Corporation 11500 N Mopac Expwy Austin, TX 78759-3504 Tel: 512-794-0100 Fax: 512-683-8411
subtotal			\$580	
TOTAL			\$55,647	

Mobility Measurements

EQUIPMENT	MODEL	UNIT PRICE	TOTALS	VENDER AND ADRESS
Nitrogen Laser	VSL-337	\$4,570		Laser Science, Inc. 8E Forge Parkway Franklin, MA 02038 Tel: 508-553-2353 Fax: 508-553-2355
subtotal			\$4,570	
High Voltage DC Power Supply	PS350	\$1,250		Stanford Research Systemes
GPIB Interface	Option 01	\$495		1290-D Reamwood Ave. Sunnyvale, CA 94089
SHV to MHV cable, 10'	Option 03B	\$50		Tel: 408-744-9040 Fax: 408-744-9049
subtotal			\$1,795	
DC Voltage Amplifier	353A	\$525		126 Baywood Ave. Longwood, FL 32750- 3426
subtotal			\$525	Tel: 407-339-4355 Fax: 407-834-3806

Power Supply for DC Voltage Amplifier	C7169	\$1,231		360 Foothill Road Bridgewater, NJ 08807- 0910 Tel: 908-231-0960 Fax: 908-231-1218
subtotal			\$1,231	
Oscilloscope	TDS684C	\$23,620		Tektronix, Inc. 27 Technology Drive Suite Irvine, CA 92618 Tel: 949-789-7200 Fax: 949-789-1366
subtotal			\$23,620	
Power Meter Sensor Head	33-0498 33-1140	\$1,495 \$1,850		COHERENT 2303 Lindbergh St. Auburn, CA 95602 Tel: 530-889-5365 Fax: 530-889-5366
subtotal			\$3,345	
Computer	Inspiron C500SV (E-VALUE CODE: 6V915-800813o)	\$1,399		Dell Computer Corporation One Dell Way Round Rock, Texas 78682 Tel: 800-626-8286 Fax: 800-365-5329
subtotal			\$1,399	
Gold Wire 99.9985%	10965	\$538	\$538	Alfa Aesar 30 Bond St. Ward Hill MA 01835-8099 Tel: (800) 343-0660
GPIO Controller GPIO Cable	777156-04 763061-02	\$600 \$85		National Instruments Corporation 11500 N Mopac Expwy Austin, TX 78759-3504 Tel: 512-794-0100 Fax: 512-683-8411
Subtotal			\$685	
TOTAL			\$37,708	

Photovoltaic Measurements

EQUIPMENTS	MODEL	UNIT PRICE	TOTALS	VENDER AND ADDRESS
Complete Calibrated Sources	63375	\$3,124		Oriel Corporation 250 Long Beach Blvd. Stanford, CT 06497-0872 Tel: 203-377-8282 Fax: 203-378-2457
subtotal			\$3,124	
Spectroradiome ter Software DC power supply Extra Battery (already included with standard system)	PR-650 SpectraWin DC-600	\$11,900 \$1,900 \$245 \$195		Photo Research, Inc. 9731 Topanga Canyon Place Chatsworth, CA 91311- 4135 Phone: (818) 341-5151

subtotal			\$14,240	
Extender Electronics Module (Phase imaging module for AFM)	PHAS-R	\$9,000		Digital Instruments/Veeco Metrology Group 112 Robin Hill Rd. Santa Barbara CA 93117 Phone: (800) 873-9750
subtotal			\$9,000	
Xenon Arc Lamp Power Supply	68811	\$2,412		Oriol Instruments 250 Long Beach Blvd. Stratford, CT 06497-0872 Tel: (203)377-8282
400 W Xenon Arc Lamp	6260	\$545		
250 W QTH lamp	6334	\$23		
Socket Adapter for QTH	66143	\$181		
Housing for 200-500 W lamps	66068	\$3,953		
Stand alone ignitor	68706 universal	\$649	\$7,763	
TOTAL			\$34,127	

Thermal Analysis

EQUIPMENT	MODEL	UNIT PRICE	TOTALS	VENDER and ADDRESS
DSC 2010 Differential Scanning Calorimetry	911300.901	\$19,000	\$19,000	TA Instruments 109 Lukens Drive New Castle, DE 19720 Tel: (302) 427-4048
Quench Cooling Acces.	900674.901	\$ 1,000	\$ 1,000	
DSC Sample Press	900680.902	\$ 2,400	\$ 2,400	
Calibrated Flow Meter	270134.001	\$ 400	\$ 400	
HP Printer	925003.901	\$ 495	\$ 495	
Thermal Analyst 5000	924500.901	\$12,900	\$12,900	
TGA 2050				
Thermogravimetric Analyzer	952400.901	\$31,000	\$31,000	
Total			\$67,195	

(Circular Polarization of Luminescence Spectroscopy)				
EQUIPMENT	MODEL	UNIT PRICE	TOTAL	VENDER AND ADDRESS
Time Interval Counter	SR620	\$ 4,950	\$ 4,950	Stanford research Systems 1290-D Reamwood Ave.
Lock In	SR830	\$ 3,950	\$ 3,950	
	SR560	\$ 1,995	\$ 1,995	

Amplifier Preamplifier Subtotal			\$10,895	Sunnyvale, CA 94089 Phone: (408) 744-9040 Fax: (408) 744-9049
Photoelastic Modulator (Modulator, driver and GPIB) Subtotal	I/FS50	\$ 2,695 \$ 1,895 \$ 95	\$ 2,695 \$1,895 \$ 950 \$4,685	Hinds instruments, Inc. 3175 N. W. Alcock Dr. Hillsboro, OR 97124 Phone: (503) 690-2000 Fax: (503) 690-3000
Monochromator Grating Fiber Coupler Fiber Cable GPIB Subtotal	CM 110 AG1200-00600- 303 AF332 AF200-0200 FC /FC-U20s CM-GPIB	\$ 1,985 \$ 200 \$ 320 \$ 200 \$ 750	\$ 1,985 \$ 200 \$ 320 \$ 200 \$ 750 \$ 3,255	CVI Laser Corporation Livermore, CA Tel: (925) 449-1064 Fax: (925) 294-7747
Glan Polarizing Prisms (x2) Polarizer Holder (x2) Polarizer Holder Quartz Retardation Plate Subtotal	03 PTA 003 07 HPP 004 07 HPR 511 02 WRQ 005	\$ 750 \$ 65 \$ 69 \$ 375	\$ 750 \$ 130 \$ 69 \$ 375	Melles Griot 1770 Kettering Street Irvine, CA 92614 Phone: (714) 261-5600 Fax: (714) 261-7790
PMT Power Supply Adapter Subtotal	H7155-21 C7169 E5776	\$ 1,291 \$ 1,231 \$ 73.92	\$ 1,291 \$ 1,231 \$ 74 \$ 2,596	Hamamatsu Corporation 360 FootHill Road Bridgewater, NJ 08807 Tel: (908) 231-0960 Fax: (908) 231-1218
Sample Compartment Spectrophotome ter Cell (x2) 1000 W Xenon arc lamp Socket Adapter Lamp Housing Power Supply Subtotal	78100 13960 6269 6162 66021 68820	\$ 772 \$ 198 \$ 619 \$ 72 \$ 2,850 \$ 3,604	\$ 772 \$ 396 \$ 619 \$ 72 \$ 2,850 \$ 3,604 \$ 8,313	Oriel Corporation 250 longbeach Blvd., P. O. Box 872 Stratford, CT 06497 Tel: (203) 377-8282 Fax: (203) 378-2457
Optical Top Vibration Isolation System Complete Shelf system Subtotal	784-659-02R 14-416-36 81-233-01	\$ 5,520 \$ 2,740 \$ 1,180	\$ 5,520 \$ 2,740 \$ 1,180 \$ 9,440	Technical Manufacturing Corp. 15 Centennial Drive Peabody, MA 01960 Tel: (978) 532-6330 Fax: (978) 531
Balance (AX12)	321-60181-13	\$ 1,830	\$1,830	Shimadzu Scientific Instruments 7060 Koll Center Parking Suite 328 Pleasanton, CA 94566

Subtotal			\$ 1,830	Phone: 1-800-482-0253 Fax: 925-462-7348
Computer (control)	Dimension L (E-VALUE CODE: 6V908- 500815o)	\$ 2,168	\$ 2,168	Dell Computer Corporation One Dell Way Round Rock, TX 78682 Tel: 800-626-8286
Subtotal			\$ 2,168	Fax: 800-365-5329
GPIB Controller GPIB Cable	777158-01 763061-02	\$ 495 \$ 85	\$ 495 \$ 85	National Instruments Corporation 11500 N Mopac Expwy Austin, TX 78759 Tel: (512) 794-0100
Subtotal			\$580	Tel: (512) 683-8411
Total			\$45,086	

Grant Total Budget: \$ 239,763